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(54) Title: MULTILAYERED SHEETS HAVING EXCELLENT ADHESION

(57) Abstract

Disclosed are multilayered sheets, preferably formed by coextrusion, comprising an outer layer of a thermoplastic polyurethane elastomer, an outer layer of copolyester, and a tie layer of a modified polyethylene. The sheets have excellent adhesion and are especially useful as a carrier for decorative and/or protective coatings.

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MULTILAYERED SHEETS HAVING EXCELLENT ADHESION

Technical Field

This invention relates to multilayered films or sheets which have excellent adhesion. More particularly, the invention relates to multilayered sheets wherein a tie layer of a particular polyethylene is used to bond layers of copolyester with a thermoplastic polyurethane elastomer. Because of the sheet having excellent adhesion, both between layers and to other substrates, it is especially useful as a carrier for decorative and protective coatings to be applied to substrates such as automobile panels.

Background of the Invention

As used herein, the term "sheet(s)" or "sheet material" includes thin film material as well as heavier sheets.

This invention, in one aspect, provides multilayered, flexible films which may be formed by coextrusion. These films have excellent adhesion. They have three or more layers and consist of at least one layer each of a flexible copolyester, a thermoplastic polyurethane elastomer and an adhesive or tie layer for bonding the copolyester layer to the polyurethane layer.

Patents of interest include U.S. Patent Nos. 4,643,926; 4,119,267; 4,210,686; 4,803,102; 4,939,009; 4,948,654; 4,910,085 and 4,349,469. The '926 patent discloses a flexible film comprising several layers of polymeric material. For example, one of the flexible films disclosed comprises a polyallomer and a flexible copolyester tied together with various tie layers (for example, an ethylene propylene copolymer, Column 4, lines 7 and 8). Applicants' invention provides unexpected improved results in adhesion using

the low molecular weight polyethylene with a flow rate of 0.25 to 40, over the tie layers disclosed by this reference. Furthermore, published technical literature by Mitsui Petrochemical Industries, Ltd., directed to Admer resins discloses the utility of low molecular weight polyethylene resins as adhesive layers between various materials including certain plastics.

Description of the Invention

According to one aspect of the present invention, there are provided multilayered films having excellent adhesion. The films are normally coextruded into three or five layered structures, i.e., A–B–C or A–B–C–B–A, wherein A is a polyurethane elastomer, B is a modified low molecular weight polyethylene resin as defined herein, and C is a copolyester.

According to the present invention, there is provided sheet material especially adapted for in–mold injection molding applications comprising a first outer layer, an intermediate tie layer and a second outer layer,

a) the first outer layer comprising a thermoplastic polyurethane elastomer,

b) the tie layer comprising a copolymer of ethylene and at least one other unsaturated monomer, the copolymer having a density of about 0.85–1.00 g/cc, and

c) the second outer layer comprising an amorphous polyester having repeat units from terephthalic acid, and at least one glycol selected from ethylene glycol and 1,4–cyclo–hexanedimethanol.

The polyurethane elastomer used in the sheet material of the present invention is preferably a thermoplastic elastomer. These elastomers are

copolymers of a hard segment and a soft segment. The hard segment is formed from an aromatic diisocyanate, examples of which are 4,4'—diphenylmethane diisocyanate and toluene diisocyanate, and a glycol or diamine chain extender (e.g., 1,4—butanediol). Minor amounts of a diamine extender may also be used. The soft segment is incorporated as a polyester or polyether polyol of molecular weight in the range of 500 to 5000. Examples of these materials are polycaprolactone polyester, polytetramethylene glycol polyether and hybrids of polyether and polyester. Such polyurethane elastomers are produced by techniques well known in the art and many are commercially available. Examples include PELLATHANE polyurethane elastomer (Dow).

The amorphous copolyester used as the second outer layer has an I.V. of 0.5—1.0, preferably 0.7, and is made using conventional polycondensation methods. Either terephthalic acid or a dialkyl ester thereof such as dimethyl terephthalate may be used as the dicarboxylic acid component. Minor amounts, up to 10 mol %, of other conventional dicarboxylic acids may be used if desired.

The copolyester also contains repeat units from at least one glycol selected from ethylene glycol and 1,4—cyclohexanedimethanol and mixtures thereof. Minor amounts, up to 10 mol %, of other conventional glycols may be used if desired.

Conventional dicarboxylic acids and glycols are identified above in the description of the polyurethane elastomers.

The tie layer used in this invention is described as a low molecular weight copolymer of ethylene having a melt flow rate of 0.25 to 40.0 g/10 min., a tensile strength at break of at least 25 kg/cm^2, a melting point of at least 65°C and a density of about 0.85—1.00 g/cc).

The tie layer is further described as a low molecular weight polymer of ethylene with about 0.1 to about 30 weight percent of at least one unsaturated monomer which can be copolymerized with ethylene, e.g., maleic acid, fumaric acid, acrylic acid, methacrylic acid, vinyl acetate, acrylonitrile, methacrylonitrile, butadiene, carbon monoxide, etc. Preferred are acrylic esters, maleic anhydride, vinyl acetate, and methacrylic acid. Many such polymers are commercially available under trademarks such as Admer AT-469C, Lotader AX-8040, Elvax 260, Bynel CXA3036 and 3101 and Lotader HX-8020.

Typically, the thicknesses of the layers are 4-20 mils for the polyurethane elastomer, 0.5-3.0 mils for the tie layer and 4-20 mils for the amorphous copolyester.

The films according to the present invention are preferably formed by cast coextrusion using conventional techniques. The sheet material of this invention may include a protective and decorative layer such as a paint layer on one of the outer layers.

The preferred manner of using the sheet material of this invention comprises the steps of providing a mold in the configuration of the shaped article; positioning within the mold the above described multilayered sheet material, injecting into the mold a fluid composition which is capable of hardening to both form the desired shaped article and bond to the sheet material (preferably polyolefin, polyester or copolyester); and removing from the mold a shaped article having a protective and decorative coating formed from the sheet material securely bonded thereto. In this instance, the sheet material is placed in a mold cavity, and a molding material, such as a polyolefin, is injected into the mold cavity under pressure against the sheet material such that the sheet material conforms to the shape of

the molded article and bonds to the outer surface of the article. Suitable molds, molding compositions and molding process parameters for this method are well known and form no part of the present invention. If desired, the sheet material may be preshaped prior to being placed in the mold. Also, conventional thermoforming techniques may be used. The film layer materials may also contain stabilizers, colorants, processing aids, glass fibers, and flame retardants.

This in-mold application of film laminates would preferably be applied to injection-molded parts which could be used in a number of applications. An example would be automobile or truck parts such as bumpers, fascia, and trim applications (flexible or rigid) such as claddings, trim strips. For applications requiring the excellent abrasion resistance of polyurethane, the film of polyurethane could be applied to a less-expensive copolyester, polyester, or thermoplastic polyolefin material. These applications would be useful for parts experiencing high wear forces or loadings such as parts for materials handling equipment, recreational equipment or vehicles.

The film laminate could also be used with reaction injection molding processes and with vacuum forming processes.

The following examples are submitted for a better understanding of the invention.

Example 1

A three-layer film laminate is coextruded from Dow PELLATHANE thermoplastic polyurethane elastomer 2103-55D for the outside Layer A, Mitsui Admer AT469C for the tie layer (Layer B), and an amorphous copolyester having repeat units from terephthalic acid, about 65-75 mol % ethylene glycol and about 53-25 mol % 1,4-cyclohexane-

dimethanol for the inside Layer C. The composition of the tie layer is a copolymer containing mostly repeat units from ethylene, having a melt flow rate (190°C) of 1.0 g/10 min, a density of 0.88 g/cm^3, a tensile strength at break of 30 kg/cm^2, an elongation at break of >500 percent, Izod impact strength of unbreakable, a D-shore hardness of 16, an A-shore sharpness of 72, a melting point of 75°C and excellent clarity. The melt temperatures are 220, 249 and 190°C for Layers A-C, respectively. Coextrusion block temperature is set at 222°C. Film thicknesses are 6, 2 and 4 mils for Layers A-C, respectively. The film is placed into an injection molding machine for molding glass fiber reinforced polyethylene terephthalate onto Layer C the film laminate. Mold temperatures are 37-40°C. The adhesive strength of the film laminate is so excellent that the peel could not be started for the peel test. The adhesive strength after molding of the 3-layer film laminate onto glass-fiber reinforced poly(ethylene terephthalate) is measured using 180° peel strength test (ASTM D903). The average peel strength is measured to be 2.0 lb/in. (36 g/mm) and peak peel strength to be 2.6 lb/in. (46 g/mm).

Example 2

A three-layer film laminate is coextruded from Dow PELLATHANE thermoplastic polyurethane elastomer 2103-55D for the outside Layer A, Dupont Bynel CXA 3101 polymer for the tie Layer B and the same copolyester as in Example 1 for the inside Layer C. Melt temperatures are 213, 250, and 201 for Layers A-C, respectively. Film thicknesses are 5.5, 2.0, and 5.0 mils, for Layer A-C, respectively. Mold temperatures are the same as for Example 1. The adhesive strength of the film laminate is measured using the 180° peel strength test

(ASTM D903). Average peel strength is measured to be 4.0 lb/in. (71 g/mm), and the peak peel strength to be 4.2 lb/in. (75 g/mm). The adhesive strength after molding of the 3-layer film laminate onto a copolyester of the same composition as Layer C and glass fiber reinforced PET is measured using 180° peel strength test (ASTM D903). The average peel strength with PETG 6763 molding material is measured to be 0.6 lb/in. (10.7 g/mm) and peak peel strength to be 2.5 lb/in. (45 g/mm). With the reinforced PET, the average is 3.8 lb/in. (68 g/mm) and peak is 7.6 lb/in. (136 g/mm).

In the above examples, from the peel strengths it can readily be seen that there is excellent adhesion between this sheet and the substrate. Also, using the protective and decorative sheet according to this invention, provides a high quality coating of attractive appearance. There appear to be no detrimental effects on the finish resulting from the molding procedure.

Whenever the term "inherent viscosity" (I.V.) is used in this application, it will be understood to refer to viscosity determinations made at 25°C using 0.50 gram of polymer per 100 mL of a solvent composed of 60 wt % phenol and 40 wt % tetrachloroethane.

The "melting point" (T_m) of the polymers described in this application are readily obtained with a Differential Scanning Calorimeter. Melt flow rate is determined by ASTM-D1238 and tensile strength is determined by ASTM-D638.

The strength of the bonds is determined by the "Peel Test" based on a modification (i.e., three test specimens) of the ASTM "T-Peel Test" set forth on pages 63 and 64 of the 1964 edition of the BOOK of ASTM STANDARDS, published by the American Society of Testing Materials, and more specifically identified as Test Number D-1876-61-T.

Unless otherwise specified, all parts, percentages, ratios, etc., are by weight.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

CLAIMS

1. Sheet material adapted for in-mold injection molding applications characterized as comprising a first outer layer, an intermediate tie layer and a second outer layer,
   a) said first outer layer comprising a thermoplastic polyurethane elastomer,
   b) said tie layer comprising a copolymer of ethylene and at least one other unsaturated monomer, said copolymer having a density of 0.85–1.00 g/cc, and
   c) said second outer layer comprising an amorphous copolyester having repeat units from terephthalic acid, and at least one glycol selected from ethylene glycol and 1,4–cyclo–hexanedimethanol.

2. Sheet material according to Claim 1 wherein said ethylene copolymer is a copolymer of ethylene with a monomer selected from maleic acid, fumaric acid, acrylic acid, methacrylic acid, vinyl acetate, acrylonitrile, methacrylonitrile, butadiene and carbon monoxide.

3. Sheet material according to Claim 1 wherein said ethylene copolymer has melt flow rate of 0.25–40 g/10 min, a tensile strength at break of at least 25 g/cm^2, and a melting point of at least 65°C.

4. Sheet material according to Claim 3 wherein said ethylene copolymer has a melt flow rate of 0.5–20 g/10 min.

5. Sheet material according to Claim 1 wherein said ethylene copolymer has a melt flow rate of 0.8—1.2 g/10 min, a tensile strength at break of 20—40 kg/cm^2, an elongation at break of greater than 50%, an Izod impact strength of unbreakable, a D—shore hardness of 14—18, an A—shore hardness of 70—74 and a melting point of 70°—80°C.

6. Sheet material according to Claim 1 provided with a decorative or protective coating on said first outer layer.

7. A molded article having sheet material according to Claim 1 adhered to one side thereof.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/08851

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B32B27/08; B29C45/14

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B32B ; B29C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[10]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP,A,0 371 743 (MITSUI PETROCHEMICAL INDUSTRIES LTD.) 6 June 1990 see claims 1,2,5	1,7
A	US,A,4 423 185 (MATSUMOTO ET AL) 27 December 1983 see column 3, line 12 - line 25 see column 6, line 63 - column 7, line 31 see abstract see column 8, line 1 - line 24	1,7
A	EP,A,0 266 107 (REXHAM CORP.) 4 May 1988 see column 6, line 55 - column 7, line 16	1,6,7
A	EP,A,0 326 355 (DU PONT CANADA INC.) 2 August 1989 see column 7, line 27 - line 40; claim 1	1,7

[10] Special categories of cited documents :

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10 MARCH 1992	24.03.92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	MCCONNELL C.H.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9108851 SA 54385

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/03/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0371743	06-06-90	JP-A- 2214650	27-08-90
		JP-A- 2234986	18-09-90
		JP-A- 2145331	04-06-90
		AU-B- 610767	23-05-91
		AU-A- 4574089	14-06-90
		US-A- 4997707	05-03-91
US-A-4423185	27-12-83	None	
EP-A-0266107	04-05-88	JP-A- 63120640	25-05-88
EP-A-0326355	02-08-89	JP-A- 2141218	30-05-90